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Evaluation of Process That Might Lead to Separation of Actinides in Waste Storage Tanks Under Alkaline Conditions

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ABSTRACT

This study addresses the physical-chemical processes that might naturally or inadvertently occur and that would lead to a separation of the poisoning nonfissionable actinides (^{232}Th, ^{238}U) from the fissionable ones (^{239}Pu, ^{235}U) by selective dissolution and redeposition over a prolonged storage of the waste. Of the various chemistries that were evaluated, carbonate complexation reaction is the most plausible means of achieving the separation of these actinides. Carbonate ions (formed by the dissolution and hydrolysis of atmospheric CO_2) can selectively dissolve the actinide oxides through the formation of soluble carbonate complexes, which could result in the separation of poisoning actinides from the fissionable ones. The concentrations of these soluble carbonate species are dependent on the pH, temperature, and other ions; therefore, changes in any of these parameters over time—especially cyclic changes (daily or seasonal)—could cause a selective dissolution and redeposition of the more soluble species away from the less soluble ones. Detailed calculations using the stability constants for the carbonates have shown that the most likely pH range for this process to occur is pH = 10–11. Increased solubility through reaction with organic complexants such as EDTA was also considered, and while it presents a situation similar to carbonate complexation and similar potential for autoseparation of the actinides in the waste tanks, it would require the uncontrolled dumping of large amounts of complexants into the storage tanks.

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INTRODUCTION

Precipitation of metal ions as a sludge is a common way to treat diluted liquid wastes. The clean supernate solution often can be discharged after a second polishing step, whereas the concentrated sludge is stored in large tanks to await a solidification treatment for final disposition. Liquid streams containing fissile materials such as enriched uranium or plutonium must be homogeneously diluted (denatured) with nonfissile materials to avoid criticality accidents. Commonly, soluble depleted or natural uranium is added before sludge precipitation to denature solutions containing fissile uranium. Similarly, thorium is added to liquid streams containing plutonium. The denaturing ratio is the ratio of chemically similar nonfissile isotopes to fissile isotopes. The ratio for uranium is $^{238}U : [(1.35 \times {}^{233}U) + {}^{235}U]$, whereas the ratio for plutonium is $^{232}Th : (^{239}Pu + {}^{241}Pu)$. An accepted denaturing ratio for uranium and plutonium is typically > 100 but was more recently increased to >200 (1). These ratios are based on the assumption that the nonfissile diluents will remain homogeneously intermixed with the fissile constituents under all conditions. This study addresses the naturally occurring or inadvertently caused physical-chemical processes that could lead to a separation of the poisoning actinides (^{232}Th, ^{238}U) from the fissionable ones (^{239}Pu, ^{235}U) over a prolonged storage of the sludge. Specifically, Th and U from Pu, and Th from U.

Chemical reactions of the tank contents causing changes in the oxidation states, hydrolysis, complexation, possible extraction into immiscible phases, and reactions with atmospheric components were all considered as they apply to wastes stored in the ORNL (Oak Ridge National Laboratory) Melton Valley storage tanks. Dissolution-reprecipitation processes are by far the most likely routes for actinides to autoseparate within the waste tanks, given the existing chemical composition. Dissolution processes would most readily be driven by complexants that might have been added during treatment and disposal processes or by contact with the environment. The most probable complexant, carbonate ion ($CO_3^=$), can be introduced in an unnoticeable fashion through contact with air, where carbon dioxide (CO_2) dissolves in the aqueous supernate phase. Continuous air sparging would only accelerate the dissolution of CO_2, with a resultant $CO_3^=$ formation (as described later in the text) (2).

Dissolution alone is not enough to effect a separation of actinides. Reprecipitation must follow in sequence. Temperature gradients provide the most probable driver for reprecipitation because solubilities will certainly be temperature dependent, allowing dissolution to take place at one temperature and reprecipitation at another (usually lower) temperature—with the resulting slow transport of the more soluble actinide away from the less soluble one. Although considerable data exist for carbonate complexation, almost no data are available for the effects of temperature on solubility. These values were estimated to assess the magnitude of this cyclic process.

To illustrate the solubility behavior of the Th, U, and Pu hydroxides in the presence of soluble carbonate at high pH values, calculations were performed using a fixed 1.0 M concentration of total carbonate species (TC).‡ The uncomplexed carbonate is distributed among three species, $CO'_2(aq)$,‡‡ HCO_3^-, and $CO_3^=$, according to the pH of the solution. The equilibria used, with their associated equilibrium constants (3), were

$$CO'_2(aq) + H_2O \rightleftarrows H^+ + HCO_3^- \qquad K_1 = 4.48 \times 10^{-7} \qquad (1)$$

$$HCO_3^- \rightleftarrows H^+ + CO_3^= \qquad K_2 = 4.69 \times 10^{-11} \qquad (2)$$

Calculated solubilities of Th, U, and Pu hydroxides and of Th-U-Pu mixed hydroxides at a 1.0 M TC over a pH range of 8–14 are presented in the following section. Values of all equilibrium species at 1.0 M TC and estimated metal hydroxide solubilities at ambient CO_2 pressure (0.00033 atm) are presented. The oxidation states evaluated were Th(IV), U(VI), Pu(IV), and Pu(VI). The U(IV) and Pu(III) species were not considered because they would be formed only under highly reducting conditions. The Pu(V) species, existing in the environment only under extremely dilute conditions would not be stable at the concentrations needed to cause a significant separation from the nonfissile species, and therefore was also not considered here.

COMPLEXATION WITH CARBONATE IONS

Solubility Behavior of Thorium(IV), Plutonium(IV), and Uranium(VI) IN 1 M Carbonate Solutions

The precipitation of metal ions as hydroxides is not a selective process. Many ions that might be present in a waste solution will co-precipitate, including Th(IV), Pu(IV), Pu(VI), U(VI), and Fe(III). The actual solubility of the precipitate will be a strong function of the degree of order in the structure (amorphous being significantly more soluble than crystalline). In general, the solubility decreases significantly as the precipitate ages because the growth of the crystal lattice is accompanied by an increase in the stability of the precipitate. For this reason, calculations of actual and relative solubilities will depend on the particular solubility products chosen (which are, in turn, related to the degree of precipitate aging). It is desirable, therefore, to estimate tenden-

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‡ TC as used here for *total carbonate concentration* should not be confused with a similar notation used by other authors to represent *total carbon* (which includes organic carbon as well).

‡‡ Where, according to the notation used by Palmer,[3] $CO'_2(aq)$ is the total dissolved CO_2, which is the sum of $CO_2(aq)$ and H_2CO_3 but does not include the ionized forms HCO_3^- and $CO_3^=$.

TABLE 1
Published Solubility Products for Th(IV), U(VI), Pu(IV), and Pu(VI) Hydroxides

	K_{sp} at 25°C					
Species	Max.	Ref.	Other	Ref.	Min.	Ref.
$Th(OH)_4(s)$	10^{-39}	4	10^{-42}	5	$^{a}4.0 \times 10^{-50}$	6
$UO_2(OH)_2(s)$	$10^{-22.15}$	7	10^{-22}	6	$10^{-23.74}$	8
$Pu(OH)_4(s)$	10^{-52}	9	10^{-56}, 7×10^{-56}	8	$^{b}10^{-63}$	6
$PuO_2(OH)_2(s)$	$10^{-22.7}$	6			$10^{-24.5}$	8

[a] Calculated K_{sp} for ThO_2
[b] Calculated K_{sp} for PuO_2

cies and display generic trends that will help investigators better understand the general behavior of these complicated systems.

Table 1 shows the range of published solubility products for Th(I), U(VI), Pu(IV), and Pu(VI), including the calculated K_{sp} values for ThO_2 and PuO_2. There are several orders of magnitude difference between the maximum and minimum published values. As mentioned, the actual solubility values will depend on the precipitation conditions and aging; however, the conclusions derived from the calculations using different sets of K_{sp} values are *qualitatively* the same. Figure 1 exemplifies the solubility of each hydroxide, Th(IV),

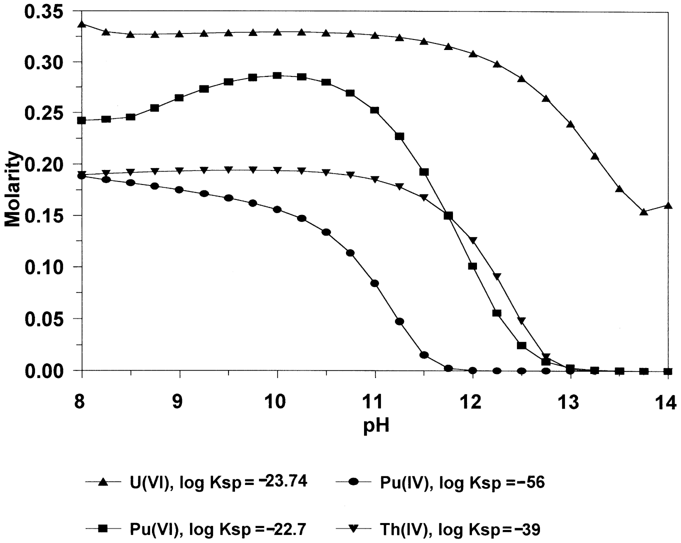

FIG. 1 Calculated typical solubility of metal hydrous oxides in a 1M carbonate solution as function of pH for Th(IV), U(VI), Pu(IV), and Pu(VI).

TABLE 2
Expressions for the Molar Concentrations, [ ], of Various Species Used in the Determination of Thorium (IV) Solubility (11–13)

(a) $[CO_3^=] = 4.69 \times 10^{-11}\,[HCO_3^-]/[H^+]$
(b) $[HCO_3^-] = 4.48 \times 10^{-7}\,[CO_2'(aq)]/[H^+]$
(c) $[Th_4^+] = K_{sp}/[OH^-]^4$
(d) $[Th(CO_3)_5]^{6-} = 2.00 \times 10^{32}\,[Th^{4+}][CO_3^=]^5$
(e) $[Th(CO_3)_5]^{6-} = 4.37 \times 10^{39}\,[CO_3^=]^5\,[H^+]^4$
(f) $[Th(OH)_3(CO_3)]^- = 3.35 \times 10^8\,[CO_3^=][H^+]$
(g) $TC = [CO_2'\,(aq)] + [HCO_3^-] + [CO_3^=] + 5[Th(CO_3)_5]^{6-} + [Th(OH)_3(CO_3)]^-$

U(VI), Pu(IV), and Pu(VI), in a 1.0 M carbonate solution using a selected representative K_{sp} value for each.

Solubility of Thorium(IV) and Plutonium(IV) Mixtures as a Result of Carbonate Complexation

The Th(IV) hydroxide is generally more soluble than the Pu(IV) hydroxide (4–10). However, the carbonate complexes of Pu(IV) are generally more stable than the thorium complexes (11–14). As a result, the solubilities of Th(IV) and Pu(IV) in a carbonate solution are comparable in the 8–10 pH range. Tables 2 and 3 show the species and equilibrium constants considered for Th(IV) and Pu(IV) in an alkaline-carbonate aqueous solution.

TABLE 3
Expressions for the Molar Concentration, [ ], of Various Plutonium(IV) Species Used in the Determination of Pu(IV) Solubility (9–19, 14)

(a) $K_{sp} = [Pu^{4+}][OH^-]^4$
(b) $[Pu(OH)_4(CO_3)_2]^{4-} = 1.99\;5 \times 10^{-3}[HCO_3^-]^2$
(c) $[PuCO_3]^{2-} = 10^{17}[Pu^{4+}][CO_3^=]$
(d) $[Pu(CO_3)_2] = 7.94 \times 10^{29}[Pu^{4+}][CO_3^=]^2$
(e) $[Pu(CO_3)_3]^{2-} = 1.259 \times 10^{39}[Pu^{4+}][CO_3^=]^3$
(f) $[Pu(CO_3)_4]^{4-} = 7.94 \times 10^{42}[Pu^{4+}][CO_3^=]^4$
(g) $[Pu(CO_3)_5]^{6-} = 3.16 \times 10^{44}[Pu^{4+}][CO_3^=]^5$
(h) $[Pu(OH)_4(CO_3)_2]^{4-} = 2.51 \times 10^{46}[Pu^{4+}][OH^-]^4[CO_3^=]^2$
(i) $[Pu(OH)_4(CO_3)_2]^{4-} = 1.047 \times 10^{-5}[CO_3^=]^2$
(j) $TC = [CO_2^1(aq)] + [CO_3^=] + [HCO_3^-]^2 + 2[Pu(CO_3]^{2+}$
$+ 2[Pu(CO_3)_2 + 3[Pu(CO_3)_3]^{2-}$
$+ 4[Pu(CO_3)_4]^{4-} + 5[Pu(CO_3)_5]^{6-}$
$+ 2[Pu(OH)_4(CO_3)_2]^{4-} + 2[Pu(OH)_2(CO_3)_2]^{2-}$

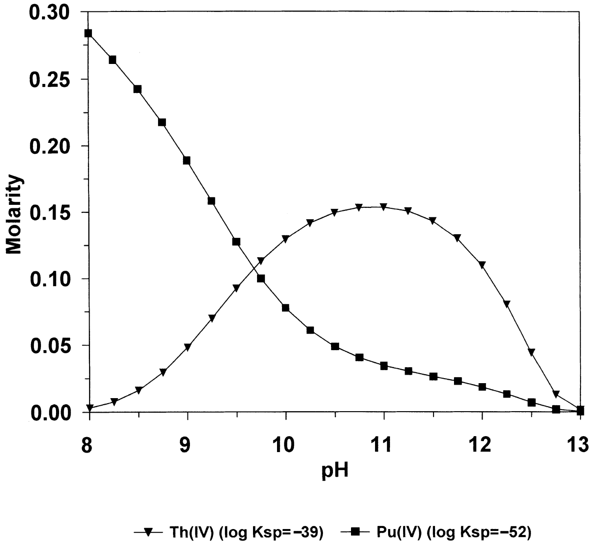

FIG. 2 Calculated solubility of Pu(IV) and Th(IV) mixtures in a 1.0 M TC solution as a function of pH.

Again, the calculated solubilities will largely depend on the K_{sp} values selected. For example, Fig. 2 depicts the calculated solubilities for Pu(IV) and Th(IV) for a combination of K_{sp} values in the presence of 1.0 M TC. The differences between the curves in Figs. 1 and 2 are due to the fact that the former is for an individual actinide, whereas the latter shows the behavior when the two actinides are present together and therefore compete for the available carbonate ion in solution. As a result of this competition, the solubilities of the two actinides are comparable only at a couple of pH values. The calculated Th-to-Pu ratio in solution will depend on the K_{sp} values used, the TC, and the pH; however, the Th-to-Pu denaturing ratio in the solid phase will change very little (2).

Combined Solubility of Thorium(IV) and Plutonium(VI) Mixtures as a Result of Carbonate Complexation

Just as in the previous case of Th(IV) and Pu(IV), the relative solubilities of Th(IV) and Pu(VI) can be compared when they occur simultaneously in solution. The Th(IV) carbonate complexes are generally more stable than the corresponding carbonate complexes of Pu(VI) as seen by comparing the related equilibrium constants for individual species in Tables 2 and 4. As a result, the solubilities of Pu(VI) and Th(IV) are comparable in the 11.5–14 pH

TABLE 4
Expression for the Molar Concentration, [ ], of Various Plutonium(VI) Species Used in the Determination of Pu(VI) Solubility (9–11, 15, 16)

(a)	$K_{sp} = [PuO_2]^{2+}[OH^-]^2$
(b)	$(PuO_2(CO_3)] = 3.98 \times 10^8[PuO_2^{2+}][CO_3^=]$
(c)	$[PuO_2(CO_3)_2]^{2-} = 3.98 \times 10^{13}[PuO_2^{2+}][CO_3^=]^2$
(d)	$[PuO_2(CO_3)_3]^{4-} = 1.585 \times 10^{18}[PuO_2^{2+}][CO_3^=]^3$
(e)	$[(PuO_2)_3(CO_3)_6]^{6-} = 3.98 \times 10^{-8}[PuO_2(CO_3)_3^{4-}]^3/[CO_3^=]^3$
(f)	$TC = [CO_2^1(aq)] + [HCO_3^-] + [CO_3^=] + [PuO_2(CO_3)]$ $+ 2[PuO_2(CO_3)_2]^{2-} + 3[PuO_2(CO_3)_3]^{4-}$ $+ 6(PuO_2)_3(CO_3)_6]^{6-}$

range. The actual Pu(VI)-to-Th(IV) ratio in solution will depend on the set of values chosen. Figure 3 gives the results of the combined calculated solubilities for Th(IV) and Pu(VI) in a 1.0 M TC solution for a set of K_{sp} values showing again that when present in mixtures the solubilities of these two actinides are comparable only at a couple of pH values. The calculated Pu(VI)-to-Th(IV) ratios depend on the particular K_{sp} values, the TC, and the pH of the solution. They do not, however, depend on the Th-to-Pu denaturing ratio in the sludge because these are saturated solutions.

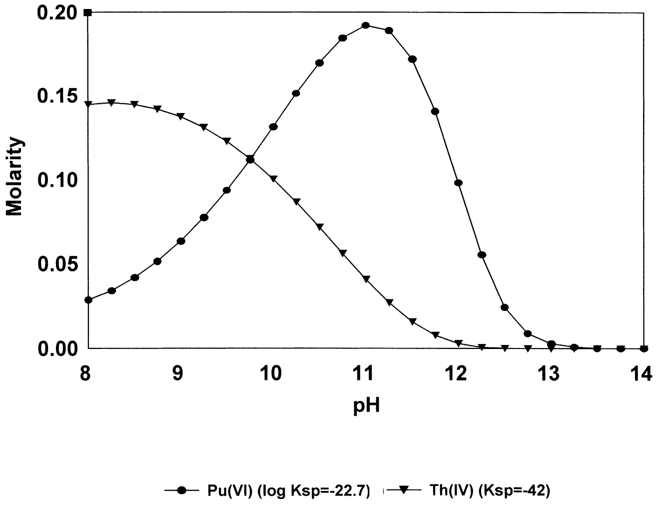

FIG. 3 Calculated solubility of Pu(VI) and Th(IV) mixtures in a 1.0 M TC solution as a function of pH.

Effect of Temperature on the Carbonate Complexation and Overall Solubilities

It is possible that a temperature gradient resulting from local, daily, or seasonal ambient temperature differences could provide a means for the transportation and separation of radionuclides (in this study, actinides) by repeated cycles of dissolution, complexation—enhanced by carbonate—and reprecipitation.

The characteristics of the precipitated hydroxide materials, particularly the degree of crystallinity, will significantly change the expected solubility. For this reason, one of the most important temperature effects will be in altering the nature of the precipitates and their solubility. The concentration and distribution of the different carbonate and hydroxide complexes will also be affected by the temperature because all the solution equilibria are a function of the temperature. The accurate prediction of all the actinide transport phenomena caused by temperature gradients occurring in the storage tanks would require significant research beyond the scope of this work.

However, assuming a given precipitate, K_{sp} value, and stability constants for the complexes in solution, it is possible to estimate the temperature effects by solving the multiple equilibrium expressions using the appropriate set of constants for the different temperatures. These calculations are not intended to predict the exact behavior in the tanks but, instead, to demonstrate the expected magnitude of the temperature effects. The data available in the literature for estimating temperature effects are scarce (17). However, one exception is that a relatively good set of thermodynamic properties is available for U(VI) species from which such temperature effects can be estimated.

The following section describes a calculation of equilibrium constants for 0° and 40°C using a given value at 25°C. Because most of the equilibrium constants (K) are measured at 25°C, the integrated van't Hoff equation is used to calculate the values at different temperatures, where ΔH is the enthalpy change for the particular reaction (dissolution, hydrolysis, complexation), R is the molar gas constant, and T is the Kelvin temperature.

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{3}$$

Table 5 gives the set of equilibrium values at 25°C and the calculated sets for 0° and 40°C. The ionization constants for water (K_w) at different temperatures were taken directly from ref. (18), whereas the temperature dependence of the CO_2–H_2O equilibria was calculated using the following equations (19):

$$\log K_1 = -356.3094 - 0.06091964 \times T + \frac{21834.37}{T} + 126.8339 \times \log T - \frac{1684915}{T_2} \tag{4}$$

TABLE 5
Calculated Temperature Effects on Uranyl Hydroxy and Carbonato Equilibria

Reaction	logK 0°C	logK 25°C	logK 40°C	ΔH (KJ/mol)	Ref.
$H_2O \rightleftarrows H^+ + OH^-$	−14.9435	−13.9965	−13.5348		18
$UO_2(OH)_2(s) \rightleftarrows UO_2^{2+} + 2\,OH^-$	−24.86	−23.74	−23.15	70	20–22
$UO_2^{2+} + CO_3^= \rightleftarrows UO_2CO_3$	8.82	8.89	8.93	4.6	24–26
$UO_2^{2+} + 2CO_3^= \rightleftarrows [UO_2(CO_3)_2]^{2-}$	16.6	16.2	16.0	−23	24–26
$UO_2^{2+} + 3CO_3^= \rightleftarrows [UO_2(CO_3)_3]^{4-}$	23.25	22.61	22.27	−40	24–26
$3UO_2^{2+} + 6CO_3^= \rightleftarrows [(UO_2)_3(CO_3)_6]^{6-}$	57.24	56.23	55.70	−63	24–26
$UO_2^{2+} + 3H_2O \rightleftarrows [UO_2(OH)_3]^- + 3H^+$	−19.5	−19.2	−19.0	18	23
$HCO_3^- \rightleftarrows CO_3^= + H^+$	−10.22	−10.33	−10.63		19
$CO_2^1(aq) \rightleftarrows HCO_3^- + H^+$	−6.30	−6.35	−6.57		19

$$\log K_2 = -107.8871 - 0.03252849 \times T + \frac{5151.79}{T} + 38.92561 \times \log T - \frac{563713.9}{T_2} \qquad (5)$$

Figure 4 shows the calculated solubility of U(VI) for all the species considered at three different temperatures (0°, 25°, and 40°C). The principal controlling factors are the decreased stability of the carbonate complexes and rel-

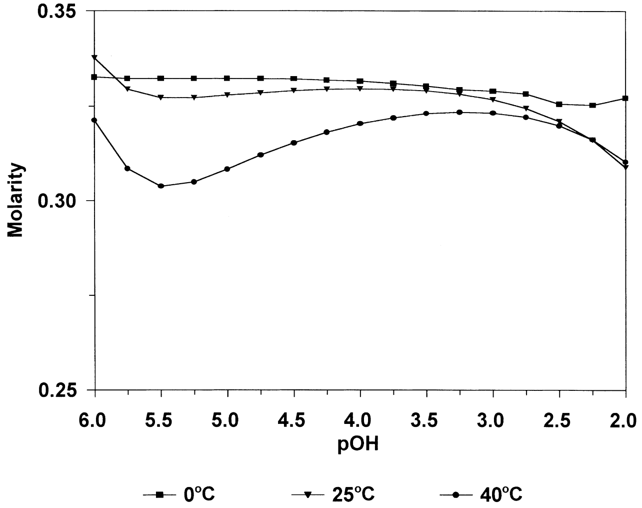

FIG. 4 Calculated U(VI) solubility in a 1 M TC solution at 0, 25, and 40°C as a function of pH.

atively lower free carbonate versus an increased solubility of the hydroxide at higher temperatures. The calculated solubility is slightly higher at lower temperatures, but the real expected behavior could be significantly more complicated and thus beyond the scope of this effort. Nevertheless, these calculations serve to demonstrate the magnitude of the temperature effect that could lead to the separation and transport of the actinides.

Similar calculations can be performed for Th(IV), Pu(IV)/Pu(VI), and for the simultaneous equilibria involving all species if sufficient thermodynamic data were available. It is expected that the magnitude of the temperature effects on these species will be similar and, therefore, a selective actinide transport resulting from temperature gradients would be the most probable actinide separation route in an unattended storage tank. A simple and inexpensive means to control the buildup of carbonate in the aqueous medium would be the addition of lime, which would precipitate $CaCO_3$, maintaining a very low concentration of carbonate ions in solution.

EDTA COMPLEXATION

The presence of significant quantities of a strong complexing agent in the storage tanks could also selectively solubilize and separate the actinides present in the sludge in a manner similar to that described for carbonate-ion complexation. As an example, the effect of ethylenediaminetetraacetic acid (EDTA) was considered. The uncomplexed EDTA species distribution was calculated using the following set of equilibria

$$[H_6(EDTA)]^{2+} \rightleftarrows [H_5(EDTA)]^+ + H^+ \qquad K = 1.26 \times 10^{-1} \tag{6}$$

$$[H_5(EDTA)]^+ \rightleftarrows H_4(EDTA) + H^+ \qquad K' = 2.51 \times 10^{-2} \tag{7}$$

$$H_4(EDTA) \rightleftarrows [H_3(EDTA)]^- + H^+ \qquad K_1 = 1.0 \times 10^{-2} \tag{8}$$

$$[H_3(EDTA)]^- \rightleftarrows [H_2(EDTA)]^{2-} + H^+ \qquad K_2 = 2.089 \times 10^{-3} \tag{9}$$

$$[H_2(EDTA)]^{2-} \rightleftarrows [H(EDTA)]^{3-} + H^+ \qquad K_3 = 7.76 \times 10^{-7} \tag{10}$$

$$[H(EDTA)]^{3-} \rightleftarrows [EDTA]^{4-} + H^+ \qquad K_4 = 6.76 \times 10^{-11} \tag{11}$$

The equations used were

$$\begin{aligned}\alpha = {} & [H^+]^6 + K[H^+]^5 + K{\cdot}K^1[H^+]^4 \\ & + K{\cdot}K^1{\cdot}K^1[H^+]^3 + K{\cdot}K^1{\cdot}K_1{\cdot}K_2[H^+]^2 \\ & + K{\cdot}K^1{\cdot}K^1{\cdot}K^2{\cdot}K^3[H^+] + K{\cdot}K'{\cdot}K_1{\cdot}K_2{\cdot}K_3{\cdot}K_4\end{aligned} \tag{12}$$

where α is the fraction of EDTA that is undissociated, that is, H_4EDTA. If FEDTA is the concentration of EDTA not complexed with the metal ions, the concentrations of the uncomplexed EDTA species are given by

$$[\mathrm{EDTA}]^{4-} = \frac{K \cdot K^1 \cdot K_1 \cdot K_2 \cdot K_3 \cdot K_4}{\alpha} \cdot \mathrm{FEDTA} \tag{13}$$

$$[\mathrm{H(EDTA)}]^{3-} = \frac{K \cdot K^1 \cdot K_1 \cdot K_2 \cdot K_3 \cdot [\mathrm{H}^+]}{\alpha} \cdot \mathrm{FEDTA} \tag{14}$$

$$[\mathrm{H_2(EDTA)}]^{2-} = \frac{K \cdot K^1 \cdot K_1 \cdot K_2 \cdot [\mathrm{H}^+]^2}{\alpha} \cdot \mathrm{FEDTA} \tag{15}$$

Solubility of Thorium(IV), Plutonium(IV), and Uranium(VI) by EDTA Complexation

Tables 6, 7, and 8 show species and equilibrium equations for the EDTA complexes of U(VI), Th(IV), and Pu(IV) (28–36). The EDTA complexes with U(VI) are significantly less stable than complexes formed with Th(IV) and Pu(IV). However, the solubility of uranyl hydroxide is relatively high when compared with Th(IV) and Pu(IV) hydroxides. The Pu(IV) complexes with EDTA are slightly more stable than the Th(IV) equivalents, but the Pu(IV) hydroxide is significantly less soluble than the Th(IV) hydroxide. As in the previous calculations, the calculated combined solubilities will depend greatly on the values chosen for the solubility products.

Figure 5 shows the results for a representative set of K_{sp} values. As can be seen, U(VI) is preferentially solubilized by complexation with EDTA in the alkaline range, whereas Th(IV) complexation is prevalent at lower pHs. The calculated solubilities for Pu(IV) complexed with EDTA are always insignificant and are not shown in these combined figures—being essentially zero over the pH range considered. It can be concluded from these results that the three actinides, having widely different solubilities of their respective EDTA complexes, could autoseparate, transport to a cooler region, and precipitate in a manner similar to that which takes place during carbonate complexation.

TABLE 6
Expressions for the Molar Concentrations, [ ], of Various Species Used in the Determination of Th(IV) Solubility Due to Complexation with EDTA (27)

(a) $K_{sp} = [\mathrm{TH}^{4+}][\mathrm{OH}^-]^4$
(b) $[\mathrm{Th(EDTA)}] = 1.585 \times 10^{23}[\mathrm{Th}^{4+}]\,[\mathrm{EDTA}^{4-}]$
(c) $[\mathrm{Th(EDTA)H}]^+ = 95.5[\mathrm{Th(EDTA)}]\,[\mathrm{H}^+]$
(d) $[\mathrm{Th(EDTA)(OH}^-)] = [\mathrm{Th(EDTA)}]/\{1.096 \times 10^7[\mathrm{H}^+]\}$
(e) $[\{\mathrm{Th(EDTA)(OH)}\}_2^{-2}] = [\mathrm{Th(EDTA)}]^2/\{6.61 \times 10^9[\mathrm{H}^+]^2\}$

TABLE 7
Expressions for the Molar Concentrations, [ ], of Various Species Used in the Determination of U(VI) Solubility Due to Complexation with EDTA (27–29, 32, 33)

(a) $K_{sp}\,[\mathrm{U(VI)}] = [\mathrm{UO_2^{2+}}]\,[\mathrm{OH^-}]^2$
(b) $[\{(\mathrm{UO_2})\mathrm{H(EDTA)}\}^-] = 2.24 \times 10^7\,[\mathrm{UO_2^{2+}}]\cdot[\mathrm{H(EDTA)}^{3-}]$
(c) $[\{(\mathrm{UO_2})\,\mathrm{H(EDTA)(OH)}\}^{2-}] = [(\mathrm{UO_2})\,\mathrm{H(EDTA)}^-]/(4.17 \times 10^5[\mathrm{H^+}]^2)$
(d) $[\{(\mathrm{UO_2})\mathrm{EDTA(OH)}\}^{3-}] = [(\mathrm{UO_2})\,\mathrm{H(EDTA)}^-]/(8.32 \times 10^{11}\,[\mathrm{H^+}]^2)$
(e) $[(\mathrm{UO_2})_2\mathrm{EDTA}] = 5.89 \times 10^{17}[\mathrm{EDTA}^{4-}][\mathrm{UO_2^{2+}}]^2$
(f) $[\{(\mathrm{UO_2})\,\mathrm{H(EDTA)(OH)}\}_2^{-2}] = 1.862 \times 10^3[\{(\mathrm{UO_2})\mathrm{H(EDTA)(OH)}\}^{2-}]$

TABLE 8
Expressions for the Molar Concentrations, [ ], of Various Species Used in the Determination of Pu(IV) Solubility Due to Complexation with EDTA (30, 32, 34–36)

(a) $K_{sp}\,[\mathrm{Pu(IV)}] = [\mathrm{Pu^{4+}}][\mathrm{OH^-}]^4$
(b) $[\mathrm{Pu(EDTA)}] = 1.259 \times 10^{26}\,[\mathrm{Pu^{4+}}][(\mathrm{EDTA})^{4-}]$
(c) $[\mathrm{Pu(EDTA)(OH)}^-] = [\mathrm{Pu(EDTA)}]\,/\,(5.25 \times 10^4[\mathrm{H^+}])$
(d) $[\{\mathrm{Pu(EDTA)(OH)}\}_2^{-2}] = [\mathrm{Pu(EDTA)}]^2\,/\,(3.39 \times 10^6[\mathrm{H^+}]^2)$

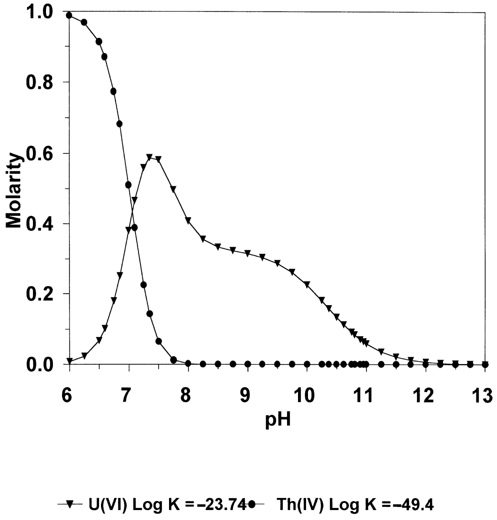

FIG. 5 Calculated solubility of Th(IV) and U(VI) mixtures in a 1.0 M total EDTA solution as a function of pH.

CONCLUSIONS

The concern that there might be some physical-chemical process that would lead to a separation of the poisoning (^{232}Th, ^{238}U) from the fissionable (^{239}Pu, ^{235}U) actinides led to this study of potential separation processes. The focus was on carbonate complexation with the three actinides as the most plausible means for separation. Temperature effects on solubility were estimated to determine the extent to which reprecipitation could occur. Under normal conditions without CO_2, the actinides exist in the sludge as hydroxy or oxide precipitates which might have undergone a significant amount of aging, resulting in further stabilization of the solids.

Carbonate ions (formed by the dissolution and hydrolysis of atmospheric CO_2) can selectively dissolve these solid actinides through the formation of soluble carbonate complexes. Uranyl(VI) is most readily dissolved, followed by Pu(VI), Th(IV), and finally Pu(IV). These soluble carbonate species are greatly dependent on pH, temperature, and other ions and, therefore, changes in any of these parameters over time, especially cyclic changes, could cause a selective dissolution and redeposition of the more soluble species away from the less soluble ones.

Detailed calculations using the stability constants for the carbonates have shown that this process is most likely to occur at $pH = 10–11$. Although temperature gradients in the waste tanks are the most probable source of such cyclic changes, temperature data for these species are not readily available. Regardless, the temperature effects on uranyl(VI) solubility illustrate that the solubility of these cations has a significant temperature dependence that can provide the driving force in a separation process that is based on dissolution/deposition through solubility differences. Correction for high solubility carbonates would be a simple matter of adding calcium ions.

Although this is the most plausible series of events that could lead to a separation of the actinides, other processes were considered as well. Increased solubility through reaction with organic complexants such as EDTA, although it presents a situation similar to carbonate complexation and similar potential for autoseparation of the actinides in the waste tanks, would first require the uncontrolled dumping of large amounts of such a complexant.

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